

Feasibility of Biogas Production from Cowpea Hull Anaerobic Digestion: Effect of Co-digestion with Waste-activated Sludge and Rice Straw

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Abstract Methane production from cowpea hull via anaerobic digestion is an environmentally friendly technique for renewable energy generation and organic waste management in Nigeria, where over half of its global production came from. However, the laboratory study on the anaerobic digestion of cowpea hull has not been sufficiently established. This study investigated the feasibility of methane production from Cowpea hull mono digestion compared to the performance of the conventional anaerobic digestion feedstock. Mono digestion of waste-activated sludge or rice straw under the same anaerobic digestion condition was set up for this purpose. Furthermore, we investigated the effectiveness of cowpea hull co-digestion with waste-activated sludge or rice straw on biogas optimization. Lastly, the optimum mixing ratio of cowpea hull to waste-activated was also quantified. Seven batch setup was subjected to 16 days of fermentation under mesophilic anaerobic conditions. Cowpea hull under mono digestion produced the highest total cumulative biogas of 203.19 mL/g-VS_{added}, followed by Rice straw (177.24 mL/g-VS_{added}). Waste-activated sludge had the least biogas 148.71 mL/g-VS_{added}. Compared to mono digestion, we realized a 27.05 % or 18.95 % optimization of biogas production from cowpea hull co-digested with rice straw or waste-activated sludge. An optimum mixing ratio of cowpea hull to waste-activated sludge was established at 3:1 (75:25) in this study. Our study is the second to investigate the bio-gasification of cowpea hull and the first to test its co-digestion and solid content characterization necessary for future investigation on cowpea hull anaerobic digestion.

Keywords: anaerobic digestion, methane, cowpea hull, co-digestion, mixing ratio

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1. Introduction

Energy plays a fundamental role in the social-economic development of any thriving society, yet residents in Nigeria have continued to endure energy deficiency. It has an estimated 13,435 MW of electricity installed capacity [1], but currently, only 15 % of the installed capacity is distributed to the end users [2]. Energy demand has intensified recently as the supply from the national grid to the over 215 million population was less than 5 GW [3], leaving 45 % of the total population or 75 % of the rural population with no access to the power grid [4]. The Nigerian government has emphasized the need to produce more energy from renewable sources to enhance energy generation. For instance, the National Renewable Energy and Energy Efficiency Policy (NREEEP, 2015) has set a long-term target of 292, 3,211, and 6,832 MW of energy from biomass, wind, and solar electricity by 2030. Biogas potential from biomass in Nigeria is estimated at around

25.53 billion cubic meter per year [6]. This potential is far higher than the NREEEP 2030 target. However, to date, Usman Danfodiyo University's 425 L biogas plant and a few other pilot systems could be found in Nigeria [6]. Moreover, laboratory study that quantifies the available biomass resource in Nigeria is limited. With the current need to devise a sustainable technology for Nigeria's growing organic waste management challenge, anaerobic digestion is increasingly receiving attention among Nigerian researchers as a sustainable disposal method for organic waste.

Organic waste, such as food waste management, is a known environmental challenge in the developed world. However, population growth and increased farming activities have been attributed to increasing organic waste management challenges in developing countries [7]. With her inefficient waste collection and disposal practice, Nigeria's situation is becoming of concern, with voluminous refuse dumping sites in many cities as clear evidence of the current situation. As of 2018, only 25% of the 32 million tons of total organic waste generated in the

country is adequately disposed of [8]. Dumping sites not only deface the cities, give off an unpleasant smell and increase the eutrophication of the water body but also contribute to the spread of malaria by harboring mosquitoes [9].

Food waste generated from low-income countries is mainly from the early and mid-stage food supply chain or post-harvest processing [10]. Reference [11] confirmed that organic waste in Nigeria comprises mainly post-harvesting and food processing waste, with a significant amount from other agricultural residues and animal waste. Rice straw (RS) and cowpea hull (CH) contribute a substantial share of the farming and food processing waste in Nigeria, respectively; specifically, the country produces 2.7×10^6 tons of rice per annum, of which 0.540×10^6 tons are discarded as rice straw [12], while it produced 3.87 million tons of cowpea seed in 2017 alone [42]. CH and rice straw are lignocellulosic biomass rich in dry matter, lignocellulosic biomass has been recognized as the most abundant renewable energy source [13,14].

CH as food waste is the outer covering of cowpea seed peeled off during the preparation of "Akara," a famous African cuisine. The high rate of CH generation in Nigeria makes it a viable substrate for bio-energy production in the form of biogas via anaerobic digestion technology. About 61 or 58 % of the annual CH output in Africa or the world came from Nigeria [15]. The seeds constitute 24.8% protein, 63.6 % carbohydrates, 6.3 % fiber, and 1.9 % fat and possess an estimated 18%, 91%, and 55 % of dry matter, organic matter, and potential methane content, respectively [16]. The high protein content in cowpea seeds implies a high nitrogen content, making the CH a potential substrate for nitrogen adjustment with other organic waste. Reference [17] investigated biogas production from CH, cow dung, and cassava peel via a locally made proto-type digester plant. After 30 days of retention time, their result showed that the highest biogas content was realized from cow dung; the methane content for cow dung, CH, and cassava peeling are 67.9%, 56.2%, and 51.4%, respectively, while the highest methane yield was gotten from CH as compared to cow dung and cassava peeling waste. However, in their study, the ambient temperature affected the biogas production rate due to the prototype digester used. As explained in the study, the outer wall of the digester is exposed to the outside environment, making it possible for the digester to lose or gain heat from the outside atmospheric temperature [17]. The fluctuating temperature might have altered a stable working condition, specifically a reduction of microbial diversity, which has been reported undesirable for the decomposition of rice straw for biohydrogen production [18]. The practical application of CH biogasification requires a model reactor to provide a conducive anaerobic working condition.

Anaerobic digestion is a relatively new technology for safe organic waste disposal with the advantage of energy recovery in the form of methane [19]. Although other effective methods for organic wastes treatment such as composting, incineration, and landfilling have been explored and are currently in practice [20,21], Access to a clean and sustainable cooking gas like bio-methane via anaerobic digestion among the rural population of Nigeria is the motivation of this study. During anaerobic digestion,

microorganisms break down their host's biodegradable materials into a gaseous form known as biogas [22]; this process begins with bacterial hydrolysis characterized by the active degradation of complex polymer to monomer by hydrolytic fermentative bacteria [23]. The major constituents of the biogas are CH₄ (55-70%) and CO₂ (30-45 %), with other minor gases like NH₃ and H₂S [24].

Furthermore, careful consideration of the various pretreatment and fermentation methods is essential in enhancing methane production efficiency from anaerobic digestion [25]. Previous studies have investigated chemical addition [26], alkalinity index [27], and thermal pretreatment [28]. While each method has favored the improvement of methane production, extra energy and a more complex process requiring more financial investment are seen in these methods [18], thus limiting their practical applicability, especially among small-scale biodigester owners.

Co-digestion of two or more feedstock with different characteristics is a cost-effective and more environmentally friendly alternative method to enhance anaerobic digestion. Reference [29] demonstrated that this technique has a synergic effect on biogas production from rice straw and sewage sludge anaerobic digestion. Enhanced biohydrogen production from co-digestion of food waste and sewage sludge has also been reported [30]. Co-digestion adjusts the total volatile solid of feedstocks with low or high carbon content [31]. While previous studies have substantially demonstrated the effectiveness of co-digestion, the feasibility of new feedstock like CH needs to be explored on the lab scale as different feedstocks have different characteristics such as carbon to nitrogen ratio and the presence of recalcitrant components in lignocellulosic materials [32]. The choice of co-digestion with rice straw and waste-activated sludge was based on similar characteristics and availability.

In addition to co-digestion, the mixing ratio of each feedstock plays a crucial role in achieving a proper anaerobic working conditions [33]. To our knowledge, no study has investigated the anaerobic co-digestion of CH in a modern-day biogas digester or its co-digestion with waste-activated sludge. This study, therefore, aims to examine the feasibility of CH application as feedstock for biogas production via anaerobic digestion technology, focusing on the effect of co-digestion and mixing ratio on biomethane production from CH. Biogas production from CH is compared with conventionally used feedstock like waste-activated sludge or rice straw.

2. Materials and Methods

2.1. Material Preparation & Characterization

This study collected and prepared three feedstocks: cowpea hull (CH), waste-activated sludge, and rice straw, followed by an anaerobic batch test. Cowpea seeds were purchased from an African grocery shop in Tsukuba. Waste-activated sludge was fetched from a wastewater treatment plant at Shimodate, while rice straw was collected from a local rice farm in Tsukuba, all in Ibaraki prefecture, Japan. For the preparation, 2kg of cowpea seeds were soaked in water at room temperature for 24

hours and gently mashed manually to peel off the outer coating (Testa). Figure 1 shows the products of the dulling process, (a) cowpea seed before dulling process, (b) CH after 24 hours soak in water. (c) cowpea seeds after removing the hull, and (d) the outer coating of cowpea seed, hereafter referred to as CH. The airdried CH was used in this study. Next waste-activated sludge was centrifuged at 4°C, 9000 rpm for 3 minutes and stored at 4°C temperature. Rice straw was cut into small sizes for easy feeding, ground (Zorojitsu electric blender) for 15 minutes, and filtered through a 1 mm sieve to achieve a consistent size. The result of the initial characteristics of all materials used in this experiment, including pH, total, and volatile solid, are presented in Table 1. Before the batch test experiment, all samples were kept in an airtight bag at room temperature to prevent contamination.

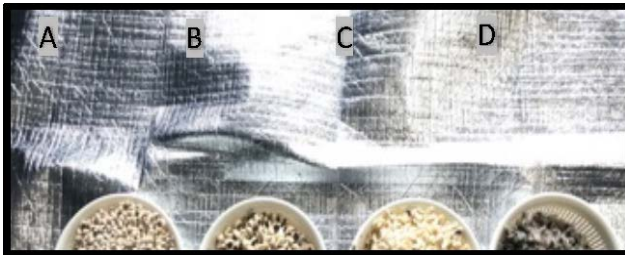


Figure 1. Cowpea seed dehulling procedures

2.2. Anaerobic Batch Test

Batch anaerobic digestion of CH using the digested sludge as inoculum was set up to investigate the feasibility of bio-methane production from first, CH mono digestion, and second, the effect of co-digestion with either WAS or RS under mesophilic anaerobic conditions. Last, we quantified the optimum mixing ratio for CH co-digestion with waste-activated sludge. A total of 7 samples (reactors) were prepared for three batch experiments. In batch 1, 2g (dry mass) of CH and 70ml of inoculum was thoroughly mixed in a beaker and added into 100 ml reactor bottles, and distilled water was used to bring the total volume to 75 ml in sample 1 (CH). Similarly, as a control experiment, an equal amount of waste-activated sludge or rice straw was mixed with inoculum in samples 2 (WAS) and 3 (RS), respectively. In the batch 2 experiment, the effect of CH co-digestion was investigated; here, 1 g of CH was mixed with an equal amount of waste-activated sludge or rice straw in samples 4 (CH/WAS) and 5 (CH/RS), respectively. In the batch 3 experiment, the optimum mixing ratio of CH to waste-activated sludge was investigated. The mixing ratio of 50/50 in sample 4 was replaced 25/75 mixing ratio for CH /waste-activated sludge was prepared in sample 6 (25:75) and 75/25 in sample 7 (75:25), respectively (based on the volatile solid content). The total mass concentration was 4 g in each 100 ml serum bottle. Next, sodium hydroxide was used to adjust the initial pH to 7.0, after which deionized water was used to bring the working volume to 65 mL in all the samples. The reactors were sealed with a silica gel stopper and air purged out with a nitrogen injector machine for 3 minutes to ensure an anaerobic working condition. Finally, all samples were placed into a mesophilic cultivator with temperature controlled at 38°C. The biogas

and bio-methane production were detected every day until the end of the fermentation on day 16 to quantify the performance of each sample. The batch experiment scenario, as shown in Table 1, was carefully repeated three times, and the average results were presented in the manuscript.

Table 1. Batch Experiments on the Biomethane Potential of Cowpea Hull (CH) and the Optimum Mixing Ratio of CH to Wasted Activated Sludge (WAS) or Rice Straw (RS)

Scenario	Substrate	CH (g)	WAS (g)	RS (g)	Mixing ratio
S1. CH	Mono-digestion	2			
S2. WAS			2		
S3. RS					2
S4. CH+RS		1		1	1:1
S5. CH+WAS(50:50)	Co-digestion	1	1		1:1
S6. CH+WAS(25:75)		0.5	1.5		1:3
S7. CH+WAS(75:25)		1.5	0.5		3:1

2.3. Analytical Methods and Kinetic Models

All feedstock and inoculum were characterized by the total solid (TS), volatile solid (VS) (Eq. (1)), and pH using standard methods [34]. The daily biogas production was monitored by air displacement using a 60 mL syringe, and methane content was quantified every two days using a gas chromatograph (GC-8A, Shimadzu, Japan) equipped with a thermal conductivity detector (80°C) and Porapak Q column (60°C) with N₂ as carrier gas. The potential of hydrogen (pH) was checked at the initial and after anaerobic digestion using a pH meter (METTLER TOLEDO Switzerland).

The modified Gompertz model was used to study the process of bio-methane production (Eq. (2)), it calculates the maximum CH₄ production potential, maximum CH₄ production rate, and lag phase as described by [35].

$$TS = \frac{M(105^{\circ}C) - Mc}{M(c+s) - Mc}, \quad (1)$$

$$VS = \frac{M(600^{\circ}C) - M(105^{\circ}C)}{M(c+s) - Mc}$$

$$P = P_{\max} \exp \left\{ -\exp \left[\frac{R_{\max} e}{P_{\max}} (\lambda - t) + 1 \right] \right\} \quad (2)$$

(1) where TS represents, the total solid; Mc, the mass of crucible; M(s+c), the mass of crucible and sample; M(105°C), the mass of the sample after drying at 105°C; M(600°C), the mass of the sample after burning at 600°C in muffle furnace; VS, volatile solid. (2) P is the cumulative CH₄ production (mL CH₄/g-VS), Pmax is the maximum CH₄ production potential (mL CH₄/g-VS), Rmax is the maximum CH₄ production rate (mL CH₄/g-VS-d), λ is the lag phase (d).

3. Results and Discussion

The result obtained in previous studies indicated that CH produces higher bio-methane compared to cow dung and cassava peel; using a prototype biogas digester, [17]

obtained the highest methane content from CH (76.2%) compared to cow dung (67.9%) and cassava peeling (51.4%). In this study, more precise biogas and bio-methane production from CH mono digestion were quantified using a more advanced batch anaerobic incubator with a temperature regulated at 38°C and an initial pH of 7.0. The result of solid content characterization followed by the effect of mono digestion, co-digestion, or mixing ratio on biogas and methane production are presented.

3.1. Solid Content Characterization of Feedstock

The solid composition of a feedstock suggests its biogas potential in an anaerobic digestion system, yet such information is not sufficiently provided in the only available study that utilized cowpea hull (CH) [17]. The summary of the characterization of all the feedstocks used in this study, including CH, waste-activated sludge (WAS), and rice straw (RS), is shown in Table 1. Cowpea has a high-solid content of 92.9 %, which is 3% higher than rice straw (89.8 %). Most of the water content in waste-activated sludge was removed by centrifugation resulting in an increased total solid of 48.5 %, unlike the uncentrifuged inoculum (10.2 %). The volatile solids in CH, waste-activated sludge, rice straw, and inoculum were 89.6, 46.3, 79.6, and 8.3, respectively, implying that most of the solids in these feedstocks are volatile solids. These characteristics indicate that in proper anaerobic working conditions, high biogas production is expected from these feedstocks.

Table 2. Characteristics of Cowpea Hull (CH), Waste-Activated Sludge (WAS), Rice Straw (RS), and Inoculum (Sewage Sludge)

Parameters	CH	WAS	RS	Inoculum
pH	ND	6.09	ND	6.98
TS (%)	92.9	48.5	89.8	10.2
Moisture content (%)	7.0	51.6	10.2	89.8
VS (%)	89.6	46.3	79.6	8.3
Dry mass (g)	5	5	5	2.5
Wet weight (g)	5.6	10.8	6.3	30.2

TS-Total solids, VS-Volatile solids, ND-No data.

3.2. Feasibility of Biogas Production from Cowpea Hull

Biogas production from cowpea hull was compared to a similar high solid and carbon-rich biomass (Rice straw) or nitrogen-rich municipal waste (waste-activated sludge), which are both conventional anaerobic digestion feedstocks that are abundantly available in Nigeria. Figure 2(a) shows the biogas production from CH mono anaerobic digestion (CH) compared to waste-activated sludge (WAS) or rice straw (RS).

After 16 days of anaerobic digestion, when biogas production dropped by less than 10 mL/g-VS_{added}, CH produced the highest amount of than waste-activated sludge and rice straw. The maximum cumulative biogas production from CH was 203.19 mL/g-VS_{added}, compared to RS (177.24 mL/g-VS_{added}). WAS accumulated the lowest amount of biogas (148.71 mL/g-VS_{added}). This implies a 12.8 % or 26.8 % more biogas production from CH compared to RS or WAS, respectively, suggesting that the mixture of CH with digested sewage sludge as inoculum resulted in an improved C/N ratio necessary for biogas production compared to other feedstocks.

The maximum cumulative methane production was obtained from CH mono digestion (Figure 3), with a maximum methane content of 71.5 % (not shown). The cumulative methane production after 16 days of anaerobic digestion was 128.4, 111.9, and 111.2 mL/g-VS_{added} for CH, waste-activated sludge, and rice straw, respectively. As shown in Figure 4, all samples recorded the highest daily methane production on the first day. Methane production on day 1 was 32.8, 39.2, and 31.0 mL/g-VS_{added} for CH, waste-activated sludge, and rice straw, respectively. Remarkably, waste-activated sludge outperformed other samples on the first day; however, daily production dropped sharply after day 1 to slightly above 5 mL/g-VS_{added} on day 5 and remained the lowest compared to other samples.

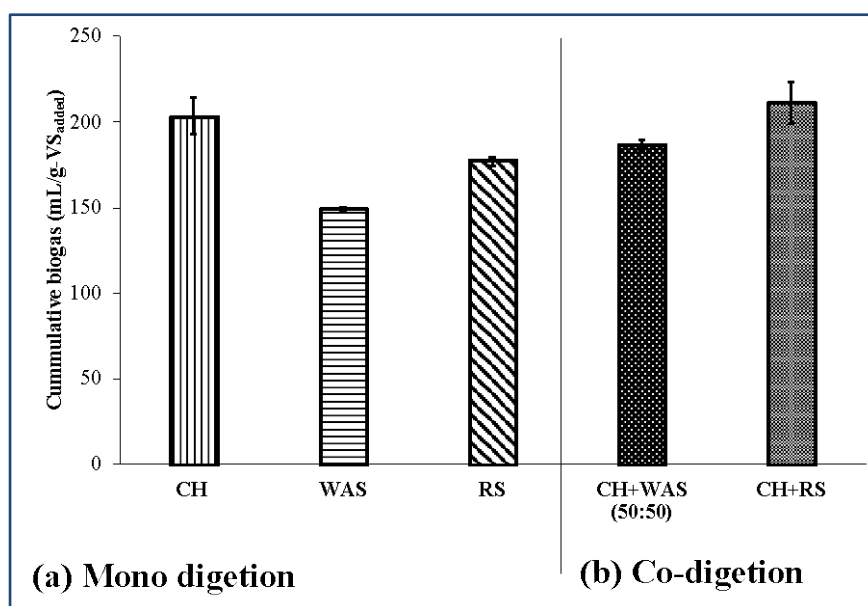


Figure 2. (a) Biogas production from the mono AD of CH (cowpea hull) waste activated sludge (WAS) or rice straw (RS), and (b) Effect of co-digestion of cowpea hull (CH) with waste activated sludge (WAS) or rice straw (RS) on cumulative biogas production

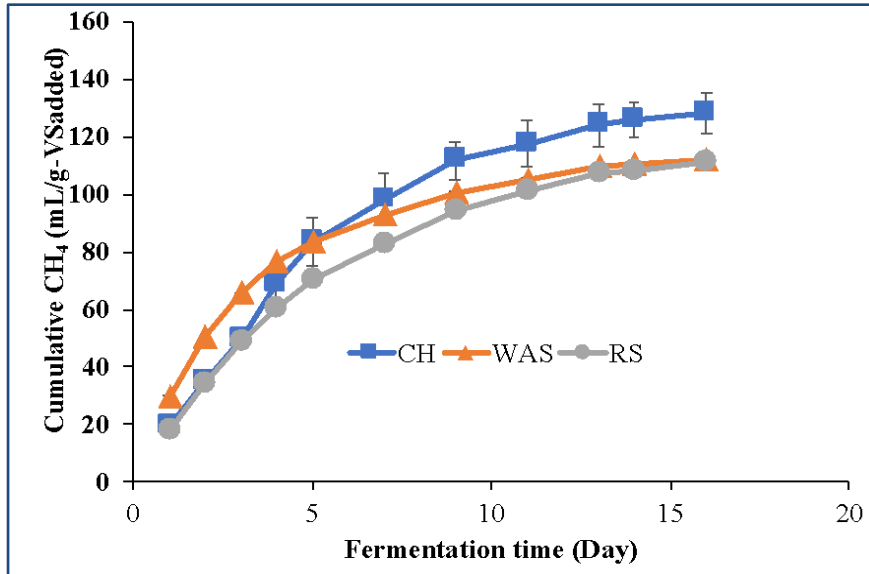


Figure 3. Cumulative methane production from CH (cowpea hull), WAS (waste-activated sludge), and RS (Rice straw) mono digestion

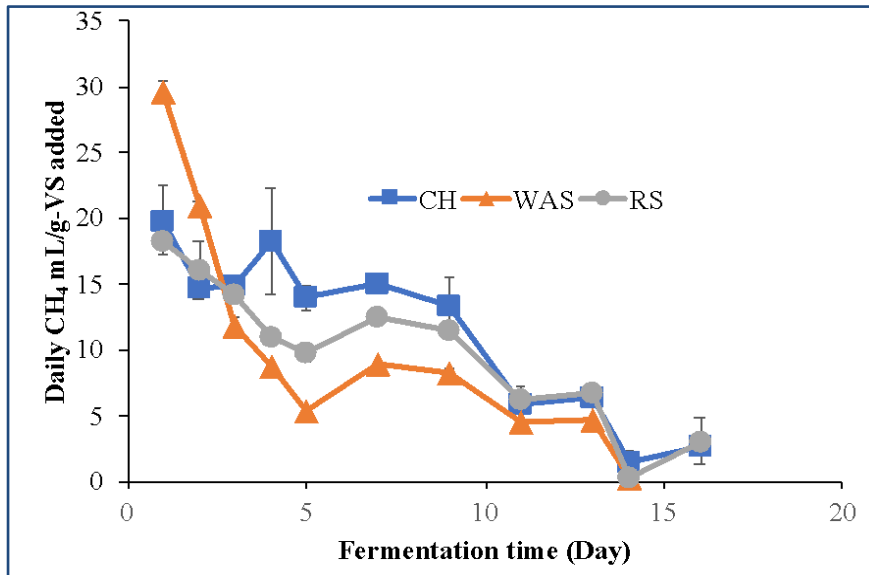


Figure 4. Daily Methane production from the mono AD of the three feedstocks. CH, cowpea hull; WAS, waste-activated sludge; RS, rice straw

On the other hand, the CH achieved a second peak on day 4, which decreased steadily with the highest daily production to the end of the digestion period. This demonstrates that CH is a promising feedstock for methane production. At the end of the digestion, WAS produced the lowest biogas among all the mono-digestion reactors in this study. WAS has a high content of nitrogen but a low amount of carbon content. The small amount of carbon in waste-activated sludge was quickly used up to produce the maximum methane production as seen on the first day, after which methane production dropped sharply, as observed in this study. Based on our literature review, we speculate that waste-activated sludge co-digestion with other carbon-rich feedstock such as rice straw or CH could optimize methane production. Co-digestion with the latter feedstock was investigated in the remaining part of this study.

3.3. Effect of Feedstock Co-digestion

In the batch 2 experiment, anaerobic co-digestion of CH with WAS or RS was examined during the 16 days of

mesophilic digestion (Figure 1(b)). The biogas production from CH+RS was 210.83 mL/g-VS_{added}, while 186.47 mL/g-VS_{added} was obtained from CH+WAS, implying an 18.95 % and 20.25 % improvement in biogas production compared to the mono-digestion of RS or WAS, respectively (Figure 1(a)). Likewise, methane production from co-digestion of CH and RS (CH:RS) was 130.45 mL/g-VS_{added} compared to 111.22 mL/g-VS_{added} from the mono-digestion of RS.

Co-digestion is considered a cheap biological method to enhance the digestion of organic waste with a rigid structure [40]. Mono-digestion of RS is known for low cumulative methane production due to its high lignin content. Reference [36] suggests that the slow depolymerization of lignin material is the limiting factor for the anaerobic digestion of lignin-containing material. However, the co-digestion of CH with RS accumulated the maximum methane production without further pretreatment. Methane production was also enhanced when waste vegetable oil was digested with pig manure [41]. Although co-digestion of CH with waste-activated

sludge produced the least amount of biogas, “WAS” was used in the subsequent experiment on the mixing ratio, as WAS is a more potential environmental challenge in Nigeria.

3.4. Effect of Mixing Ratios

To optimize the synergic effect of co-digestion of two feedstock, the impact of the mixing ratio of cowpea hull (CH) and waste-activated sludge was conducted in two sets of experiments to find the appropriate mixing ratio. CH and waste-activated sludge were mixed at 0.3, 1, and 3 ratios based on the volatile solid for reactor 25:75, 50:50, and 75:25, respectively. Figure 4 shows the effect of the CH mixing ratio to waste-activated sludge (WAS) on cumulative biogas production. CH to waste-activated sludge ratio of 3 (75:25) produced the maximum biogas, 188.93 mL/g-VS_{added}, followed by a mixing ratio of 1 (50:50) and 0.3 (25:75), which had 186.47 and

148.73 mL/g-VS_{added}, respectively. This result shows that biogas production improved by adding more CH.

Daily methane production from co-digestion of CH and waste-activated sludge (WAS) at different mixing ratios (Figure 5) shows that the maximum daily methane was produced on day 1. Methane production on day 1 was 20.90, 30.00, and 24.24 mL/g-VS_{added}, for the mixing ratio of 0.3, 1, and 3, respectively. Until day 16, when the anaerobic digestion was completed, methane production decreased steadily in all the reactors. Reference [37] achieved the highest methane production at a mixing ratio of 2 from the co-digestion of water hyacinth and banana peels. Compared to the mixing ratio of 1, improved biogas production in the mixing ratio of 3 (75:25), as found in this study, shows that an optimum anaerobic working composition was achieved at this ratio, which synergized to enhance biogas production for CH co-digestion with waste-activated sludge in this study.

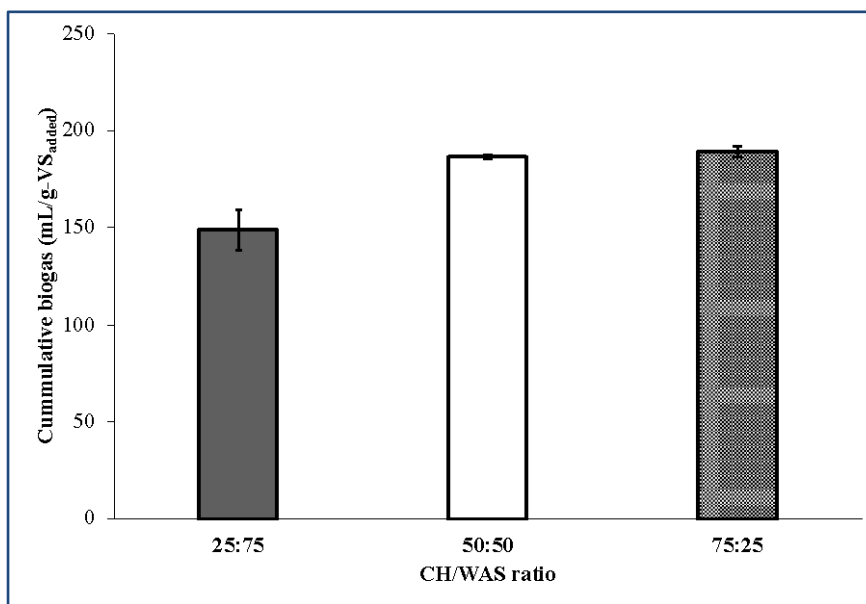


Figure 5. Effect of mixing ratio of CH (cowpea hull) to waste activated sludge (WAS) on cumulative biogas production

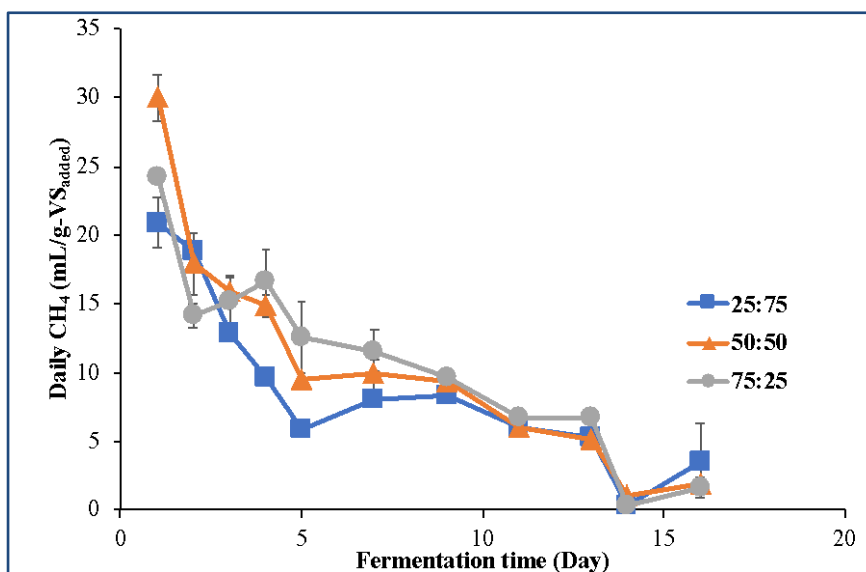


Figure 6. Daily Methane production from co-digestion of CH (cowpea hull) and waste-activated sludge (WAS) at different mixing ratios

Reference [38] also obtain achieved a similar result with the highest biogas production of 113.92 ± 6.90 mL when *Salvinia molesta* was mixed with rice straw in a ratio of 40:60. In contrast, another study showed that increasing the rice husk ratio to food waste resulted in low biogas production [33]. Conventionally food waste contains high moisture in the range of 48-95% [39]. However, the CH used in this current study has a much lower moisture content of 7 %. Therefore, an investigation of the carbon to nitrogen ratio in CH is recommended to fully understand the appropriate ratio for its co-substrate with another feedstock.

4. Conclusions

Cowpea hull demonstrated higher biogas and bio-methane production than waste-activated sludge or rice straw, which are both conventional anaerobic digestion feedstocks. Although CH has similar solid content to rice straw, it outperformed rice straw in this study, possibly due to its higher nitrogen content, while rice straw has higher lignocellulosic material like lignin, which is reported to be difficult to degrade in an anaerobic digestion system. Mono digestion of waste-activated sludge produced the least amount of methane owing to its low solid content and a corresponding low C/N ratio, thus suggesting a co-digestion with high solid feedstock. But contrary to our assumption, RS was a better co-substrate for anaerobic co-digestion with CH than waste-activated sludge in this study. Notwithstanding, we found an optimum mixing ratio of 75:25 (3:1) for CH co-digestion with waste-activated sludge.

Anaerobic digestion technology promises a unique advantage to Nigeria as an environmentally friendly means for disposal of her growing food waste and offers ample opportunity to generate clean energy in the form of methane. There is a need for more academic study in this field to properly inform the government and other stakeholders of the available opportunities in this technology, the co-benefits, and the national resource availability for large-scale exploitation. Our study investigated the feasibility of biogas production from CH and the effect of co-digestion with waste-activated sludge or rice straw. Our findings provide basic information such as the solid content characterization of CH, biogas potential under a proper anaerobic working condition, the effect of co-digestion with either waste-activated sludge or rice straw, and the optimum mixing ratio with the former. We acknowledge that other important factors play a crucial role in anaerobic digestion configuration that needs to be investigated in CH, such as the C/N ratio, volatile fatty acids content, and microbial community. This study is the second to examine cowpea hull bio-gasification and the first to provide the essential characterization necessary for future investigation on this feedstock.

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